Impacts of a Soda Ash Facility on Onondaga Lake, New York By Steven W. Effler and David A. Matthews

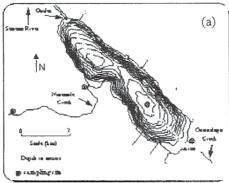
Introduction

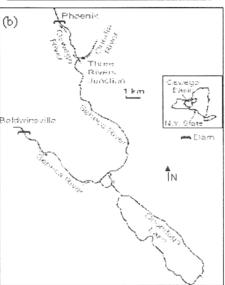
The array of impacts of industrial operations on the ecology and water quality of receiving fresh waters is nearly as varied as the myriad of wastes of industry. In extreme cases, the inputs may be manifested through conspicuous modifications of fundamental chemical and physical processes, biological community structure, and thereby overall ecosystem metabolism. This article presents a selective summary of an analysis (Effler and Matthews 2003) of the impacts of the operation of a soda ash (Na₂CO₃) manufacturing facility on Onondaga Lake, New York, its tributaries, and the river that receives the lake's outflow, with particular emphasis on the effects of ionic waste. The analysis presented here is based on an ongoing, long-term program of monitoring, process studies, and modeling (Effler 1996), conducted by the Upstate Freshwater Institute.

Onondaga Lake

Onondaga Lake is located north of the city of Syracuse, New York. The lake was oligomesotrophic (low to medium level of productivity) before European settlement in the late 1700s (Rowell 1996). Salt springs adjoining the lake were described in Jesuit publications in the mid-1600s, following exploration of the region by French missionaries. Springs were found on the banks of the lake halfway up the eastern shore and around the southern end to a tributary (Ninemile Creek) on the western shore (Clark 1849; Figure 1a). A salt rendering industry began in the late 1700s and was a major source of salt for colonial America. This industry adjoined the lake and was largely responsible for the growth of Syracuse from the late 1700s through the 1800s. The extent to which the lake was enriched with salt in this era is open to some debate. Various anecdotal observations (e.g., Clark 1849) indicate that lake concentrations were low compared to the adjoining salt springs.

The lake has a surface area of 12 square kilometers, a volume of 1.31 x 10⁸ m³, a mean depth of 10.9 meters and a maximum depth of about 19.5 meters. The two largest tributaries, Ninemile Creek and Onondaga Creek, together account for approximately 65 percent of the annual inflow to the lake (Effler 1996). The third largest inflow is from the Onondaga County Metropolitan Sewage Treatment Plant (Metro), which, on an annual average basis, contributes approximately 20 percent of the water reaching the lake. The lake is presently hypereutrophic (extremely productive) because of the very high load of phosphorus received from Metro. The lake flushes rapidly, an average of about four times per year on a completely mixed basis (Effler 1996), and thus responds rapidly to changes in





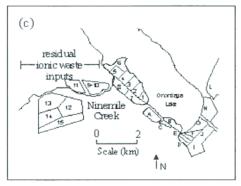


Figure 1. Areas impacted by soda ash (Na₂CO₃) production: (a) Onondaga Lake, bathymetry and inflows, (b) the Seneca and Oswego Rivers from Baldwinsville to Phoenix, and (c) distribution of waste beds (numbered or lettered) adjoining Onondaga Lake and Ninemile Creek

pollution inputs. Onondaga Lake discharges through a 1200-meter channel to the Seneca River, which, after combining with the Oneida River, becomes the Oswego River and enters Lake Ontario at the city of Oswego (Figure 1b).

Soda ash and waste production by the Solvay Process

Na₂CO₃ production

In 1865, Ernest Solvay developed the Solvay Process to produce soda ash (Na₂CO₃; used in the manufacture of glass, soap, and paper) from calcium carbonate (CaCO₃) and sodium chloride (NaCl). The process is rather complex; the overall (e.g., net) simple reaction is CaCO₃ + 2 NaCl→Na₂CO₃ + CaCl₂. The abundance of the reactants in the Syracuse/Onondaga Lake area in the form of limestone (CaCO3), and NaCl brines and deposits (Effler 1996), and the proximity of the lake for disposal of wastes and as a source of cooling water, made the shores of the lake an ideal location for the production of soda ash by this process. The Solvay Process Company (later known as Allied Chemical Company, now owned by Honeywell) began production on the western shore of Onondaga Lake in 1884. Originally, the NaCl brine was taken from the springs bounding the lake. However, the industrial demand soon exceeded the yield of these local sources. By the late 1880s, salt beds had been traced 36 kilometers southward in the Onondaga Creek watershed. The soda ash manufacturer began solution mining of NaCl brine at this site starting in 1889

Production of Na₂CO₃ increased progressively from about 70 thousand metric tons annually by 1890 to nearly 900 thousand metric tons in the mid-1960s (Figure 2). In 1971, there were 11 Solvay Process soda ash production facilities in the U.S.; this was the last operating facility. The facility ceased production of Na₂CO₂ in February 1986. During the decade before closure, about one billion gallons of nearly saturated brine was produced at the solution mines and conveyed to the facility (Effler 1996). The availability of brine and byproducts of soda ash reactions lead to diversification in chemical manufacturing; more than 30 chemicals were produced at the facility over its 102-year tenure. (Only impacts of Na₂CO₃ manufacturing are considered here.)



Figure 2. Time-series of annual production of soda ash (Na₂CO₃); and ionic waste (NaCl + CaCl₂) over the 1890 to 1985 interval.

Cooling water and Solvay waste

Cooling water for the Solvay Process was taken from deep layers of the lake. Heated water was discharged via two pathways: (1) directly to the lake along the west shore, and (2) into Ninemile Creek (and subsequently the lake; Figure 1). These releases were discontinued in the late 1970s and replaced with a multiport diffuser discharge (900 meters offshore at a depth of 4.6 meters).

Large quantities of waste were produced by the Solvay Process. A waste slurry (5 to 10 percent suspended solids [Blasland & Bouck Engineers 1989]), containing high concentrations of Cl⁻, Na⁺, Ca²⁺, excess CaO, unreacted CaCO₃, CaSO₄, and lime impurities, was pumped to "waste beds" where the soluble fraction (waste bed overflow) drained off and entered the adjoining receiving waters. The solid phase left behind after drainage of the waste bed overflow is described as Solvay waste. Deposits of this waste surround approximately 30 percent of the lake (Figure 1c). An area of more than 8.1 square kilometers is covered with this material (Effler 1996). Waste bed overflow material entered the lake directly until 1944; thereafter, it was received in the Ninemile Creek inflow to the lake (Figure 1c).

Ionic waste

The waste bed overflow was enriched in Cl⁻, Na⁺, and Ca²⁺ (Effler 1996). The USEPA (1974) described the production of ionic waste from this manufacturing facility as a nearly stoichiometric relationship with production of Na₂CO₃; for each kilogram of Na₂CO₃ produced, approximately 0.5 kilograms of NaCl and 1.0 kilogram of CaCl₂ (i.e., 1.5 kilograms of ionic waste) was discharged. This stoichiometry has been applied to the historic annual Na₂CO₃ production values to estimate the historic generation of ionic waste from this facility (Figure 2; right side Y-axis).

The ionic waste entered the lower portions of Ninemile Creek (and subsequently the lake) from Solvay wastebeds over the 1944 to mid-May 1981 interval. Starting in May 1981, a portion of the waste was diverted to Metro (4.6 kilometers to the southeast, Figure 1a) to precipitate phosphorus (tertiary treatment). This increased the points of entry of the ionic waste but did not substantively change the amount received by the lake. The estimated loading of Cl^- , Na^+ , and Ca^{2+} to the lake (based on direct monitoring of inputs) over the last 12 years of operation of the Na₂CO₃ facility (1974 to 1985) was 1.2 million metric tons (Effler et al. 1996). This nearly matched (within eight percent) the value obtained by applying the 1.5 kilograms of ionic waste per kilogram of Na₂CO₃ stoichiometry (USEPA 1974) to the soda ash production levels for the period (Figure 2).

Loading of Cl⁻ (Figure 3), Na⁺, and Ca²⁺ decreased abruptly following closure of the facility; by 1989, the annual loads of these constituents had decreased by 79, 67, and 70 percent, respectively. However, residual ionic waste loading has persisted, manifested as systematically higher concentrations of each of the three ions

in Ninemile Creek below the waste beds compared to upstream of the beds (Figure 1c), and the maintenance of the unique ion ratios of the ionic waste from Solvay Process (Effler et al. 1991, 1996). By 1989, approximately 55 percent of the total external Cl⁻ load to the lake had its origins as soda ash waste (Effler et al. 1996). By 2000, the residual Cl⁻ loading from Ninemile Creek had decreased further, representing more than 30 percent of the total load (Matthews and Effler 2003). The estimated total residual Cl⁻ load received from the waste bed area since closure of the industry through 2000 was about one million metric tons, corresponding to about 1.6 years of the full operating load before closure.



Figure 3. Time-series of annual Cl loading to Onondaga Lake for the 1971 to 2000 interval, from monitoring of inputs

Lake concentrations—Salinity

The concentrations of four cations (Ca²⁺, Mg²⁺, Na⁺, R⁺) and three anions (HCO₃⁻, SO₄²⁻, and Cl⁻) essentially constitute the total ionic salinity of most fresh waters, as other ions are usually present in much lower concentrations. Chloride, Na⁺, and Ca²⁺, the constituents of the ionic waste from soda ash production, were, and continue to be, the dominant components of salinity in Onondaga Lake. The summertime contribution of these three ions decreased from more than 85 percent to less than 70 percent following closure of the soda ash facility (Effler 1996).

). The concentration of Cl⁻ ([Cl⁻], mg/L⁻¹) is a good surrogate measure of salinity (parts per thousand, ‰) in Onondaga Lake (Effler 1996). The long-term trend in salinity for the lake, represented as the annual average volume-weighted values (from weekly [Cl-] profiles for the April to October interval and morphometric data), is presented for the 1968 to 2000 period (Figure 4). The average salinity for the monitored interval before closure of the soda ash facility was 3.0 %. The average for the four years following closure (1987 to 1990) decreased to 1.32 % (Figure 4), a reduction of more than 55 percent. Further modest decreases have occurred since 1990 (Figure 4), consistent with the additional decreases in residual loading of ionic waste. The average salinity for the 1997 to 2000 interval was 1.18 %, representing an 11 percent decrease from the 1987 to 1990 interval.

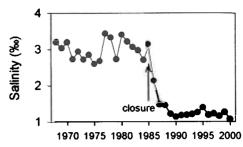


Figure 4. Long-term variations in salinity (S, volume weighted averages for the May to September interval of each year) in Onondaga Lake over the 1968 to 2000 interval (modified from Effler 1996)

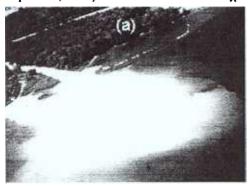
Two earlier analyses (O'Brien & Gere 1973. Rooney 1973), based on limited data, concluded the soda ash facility's contribution to the Cl concentration (i.e., salinity) in the lake before closure was only 50 to 60 percent. A subsequent analysis indicated the contribution from the facility was much higher, approximately 80 percent, based on the results of a Cl mass balance analysis (Effler and Driscoll 1986). In-lake Cl concentrations decreased 71 percent following closure of the industry, establishing that the facility's contribution to lake salinity was substantially more than the earlier estimates of O'Brien & Gere (1973) and Rooney (1973). Application of a completely mixed dynamic Cl mass balance model, developed and validated for Onondaga Lake by Doerr et al. (1994), for the case of elimination of residual ionic loading, predicted that 85 percent of the preclosure Cl concentration was attributable to the ionic waste discharge from the soda ash facility.

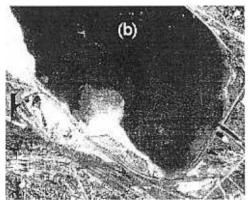
Calcium chemistry

CaCO₃ precipitation

Unlike Cl⁻ and Na⁺, Ca²⁺ is highly reactive in alkaline waters such as Onondaga Lake. The entire water column of Onondaga Lake was found to be oversaturated with respect to the solubility of calcite (CaCO₂) over the spring to fall interval before closure of the soda ash facility (Effler and Driscoll 1985), indicating a continuous tendency for the precipitation of calcite, and, once formed, no tendency for dissolution. These extraordinary conditions have been attributed to the very high concentrations of Ca2+ maintained in the lake from the ionic waste discharge (Effler and Driscoll 1985). Precipitation of CaCO₃ within the water column has been manifested in multiple ways. Yin and Johnson (1984) reported calcite particles as the dominant inorganic particle type in the lake in the early 1980s. Womble et al. (1996) reported CaCO3 as the primary component and principal regulator of the dynamics of total solids deposition in the lake; CaCO₃ represented approximately 70 percent of the total solids deposition before closure of the soda ash facility. The deposition rate of total solids reported for the early to mid-1980s (21,800 mg_m⁻²_d⁻¹) was higher than found in the literature for lakes as a result of the very high deposition rates of CaCO₃ driven by the Ca²⁺ loads from the soda ash facility.

The Ca²⁺ discharge from the soda ash facility has altered the character and quantity of both the near-shore and pelagic (deep water) sediments of Onondaga Lake. A large delta of soft sediment, composed mostly of CaCO₃, formed at the mouth of Ninemile Creek in response to the input of these particles from this stream (Figure 5a) that carried the ionic waste. The near-shore zone adjoining the manufacturing site, along the southwestern shore, has the character of the Solvay waste beds (Figure 6); it is composed mostly of calcium minerals and has a relatively impervious, "crusty" nature.





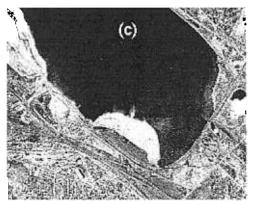


Figure 5. Aerial photographs of Onondaga Lake: (a) turbid inflow from Ninemile Creek, summer 1969, (b) turbid water plume and shoreline waste beds, September 6, 1938, and (c) turbid water plume and shoreline waste beds, October 15, 1951

The greatest portion of the near-shore zone (approximately 60 percent) is covered with concretions known as oncolites (Figure 6). These concretions are composed mostly of CaCO3 (92 percent) and range in size from a few millimeters to as much as 15 centimeters in diameter (Dean and Eggleston 1984). Dean and Eggleston (1984) contend that the formation of oncolites in Onondaga Lake is a result of the Ca²⁺ enriched ionic waste discharge, and that these concretions started to form in the lake when the ionic waste was introduced. Oncolites have a "stone-like" appearance, but have low density. Thus, they are highly susceptible to movement associated with normal wave action. The near-shore sediments adjoining the point of entry of Onondaga Creek are enriched with clay minerals (Figure 6, Effler 1996), consistent with the particularly high load of mud boil material.

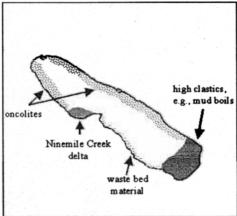


Figure 6. A generalized surficial sediment map for the near-shore zone of Onondaga

There is certainty that the discharge(s) of the soda ash facility increased sediment deposition in the pelagic (deep-water) zone of the lake (Rowell 1996, Hairston et al. 1999), and thereby accelerated the filling-in of the lake. A wide range of markers (chemical and biological) has been used in investigations of the lake's sediments to date sediment horizons, and thereby estimate sediment accumulation rates. Particularly high accumulation rates were reported for a portion of the interval of operation of the shoreline waste beds (Hairston et al. 1999), indicating impact from the direct inputs from these disposal sites. Hairston et al. (1999) speculated that the slightly shallower saddle between the north and south lake basins (Figure 1a) exists solely because of deposition from the operation of these adjoining waste beds. Turbid water plumes (presumably of CaCO₃ precipitate) were apparent in aerial photographs of the southwest corner of the lake in 1938 (Figure 5b) and 1951 (i.e., after the shift to Ninemile Creek waste beds; Figure 5c), indicating localized deposition associated with soda ash production, even after beds adjoining the lake were no longer used (Figure 5c).

Impacts on the lake's biological communities

The soda ash facility, during its operation, strongly impacted the structure (composition) and function of various biological communities of Onondaga Lake. It's noteworthy that USEPA (1974, p.34) provided early speculation on the importance of the lake's salinity on biological diversity: "The chloride/salinity levels of the lake approach concentrations at which one would expect to find the smallest species diversity; that is, the chloride/salinity level is near the upper limit for freshwater organisms and near the lower limit for marine species."

Coprecipitation of phosphorus with CaCO₃ may serve as a natural control mechanism for eutrophication in some calcareous lakes by essentially competing with phytoplankton for available forms of this critical nutrient. However, this potential benefit of the Ca2+ waste input to Onondaga Lake was probably more than compensated for by the artificial cycling of hypolimnetic (bottom water) accumulations of phosphorus to the upper productive layers during summer associated with the cooling water operation for soda ash production. Further, under the nutrient-rich conditions that prevailed in the lake, the greater deposition losses of phytoplankton (microscopic plants of the open waters) caused by the soda ash discharge (Effler et al. 2001) exacerbated (stimulated) the lake's problem of high primary production (e.g., excessive phytoplankton growth). Shifts in the diatom (type of phytoplankton) community, documented in Rowell's (1996) study of the lake's sediments, depict substantial impacts of the elevated salinity caused by the facility's ionic waste on the composition of the lake's phytoplankton community.

Through stratigraphic analyses of sediments, Hairston et al. (2003) documented the changes in an important component of the lake's zooplankton (small animals of the open waters) community (daphnids) over the late 1800s to late 1990s interval. The daphnia assemblage of the lake shifted from species typical of freshwater lakes in central New York to salinity-tolerant exotic species in the early 1900s, during a period of increasing ionic pollution and lake salinity. The daphnia population shifted back to native forms after closure of the soda ash facility (Hairston et al. 2003). Following closure of the soda ash facility, zooplankton species richness increased from 8 (generally salinity tolerant forms) to 18 common species, and included salinity intolerant natives that are more efficient grazers (consumption of phytoplankton). The abrupt, dramatic shift in the zooplankton population has been attributed primarily to the corresponding reduction in salinity, and perhaps secondarily to the attendant decreases in CaCO3 precipitation, following closure of the soda ash facility (Siegfried et al. 1996). The return of the native zooplankton resulted in improved water clarity following closure (Siegfried et al.1996), and may also have been responsible for the coincident return of late summer nuisance blooms of filamentous cyanobacteria (blue green algae, less edible than forms replaced) not observed in the lake since the early 1970s.

The soda ash facility negatively impacted the macrophyte (aquatic plants, mostly rooted) community of the lake through increases in salinity, alteration of the near-shore sediments, and perhaps high rates of CaCO3 precipitation on plant surfaces (Madsen et al. 1996). Historic (pre-1940) species richness, based largely on anecdotal observations and limited collections, was estimated to be about 15 (Madsen et al. 1996). A 1991 survey found that only 13 percent of the littoral (near-shore) zone had aquatic plants, and that the macrophyte community was limited to five submerged species (Madsen et al. 1996). The survey results indicate the plants have difficulty in establishing and remaining on oncolite sediments compared to other sediment types because of the susceptibility of these concretions to movement in normal wave action (Madsen et al. 1996). Further, a number of common macrophytes are not tolerant of the salinity that prevailed during the operation of the facility. A resurvey of the macrophyte community in 2000 demonstrated an areal expansion within the littoral zone, and an increase in species richness of only 1 (Madsen, personal communication), supporting the position that the soda ash facility negatively impacted this community. The degradation of the near-shore sediments by the soda ash facility (Figure 6) doubtless limits the recovery of this community and associated habitat.

A survey of the wave-zone benthic community (bottom dwelling animals) of the lake in 1989 found the species diversity to be unusually low, composed of forms known to be tolerant of pollution, including high salinity (Wagner 1998).

Alteration of near-shore deposits from soda ash production is at least one factor responsible for the degraded character of the lake's benthic community (Wagner 1998). Historic data on the lake's fish population are too meager to definitively establish impacts from the soda ash facility. However, it is likely the high salinity levels during operation of the facility drove many fish from the lake since most freshwater fishes have low tolerances for high salinity levels.

Synthesis/management perspectives

The geographic range of substantial impact of the soda ash facility on surface water ecosystems in central New York is impressive, extending about 35 and 5 kilometers upstream from the mouths of the two major tributaries of Onondaga Lake, throughout the lake itself, and about 3 kilometers upstream from the lake inflow to the Seneca River to about 15 kilometers downstream. Though a number of the impacts of this facility were identified before closure (Effler 1987), the range, magnitude, and implications of certain of the effects described here were only resolved by the changes brought about by the closure of this industry. The extremely high loads of ionic waste, composed of Cl⁻, Na⁺, and Ca²⁺, had major impacts on the fundamental chemical and physical properties of the lake and adjoining portions of the river system. These impacts on the chemical and physical properties of these systems in turn have had profound effects on the structure and function of the biological communities of these ecosystems.

Closure of the soda ash facility has resulted in dramatic improvements in water quality and ecological characteristics of the lake and river system, including: (1) reduction in the salinity level of the lake and downstream waters, (2) return to a more normal mixing and stratification regime in the lake, (3) reduction in the summer heat content of the lake, (4) reduction in the period of hypolimnetic anoxia, (5) clarity maxima higher and of greater duration in the lake, (6) reduction in net sediment accumulation rate, (7) reduction in the deposition rate of phytoplankton biomass, (8) increased diversity of the zooplankton community (and probably others communities) of the lake, (9) reductions in the longitudinal extent of salinity-based density stratification and coupled severely depleted dissolved oxygen conditions in the adjoining river system, and (10) increased coverage of the near-shore zone of the lake with macrophytes. The substantial residual ionic waste loading that has continued following closure was not anticipated; thus, a number of the impacts have been ameliorated, but not eliminated.

Steven W. Effler is the director of research and David A. Matthews is a research scientist at the Upstate Freshwater Institute in Syracuse, New York. The authors are actively involved in research on Onondaga Lake, its tributaries, and the Seneca River.

References will appear on NYWEA website